X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF INTERACTION OF Np^{5+} WITH GOETHITE α-FeOOH

by

Yury A. TETERIN[1], **Stepan N. KALMYKOV**[2], **Alexander P. NOVIKOV**[3],
Yury A. SAPOZHNIKOV[2], **Labud VUKCHEVICH**[4],
Anton YU. TETERIN[1], **Konstantin I. MASLAKOV**[1], **Igor O. UTKIN**[1],
Ikule B. Hasanova[2], **and Natalia S. SHCHERBINA**[2]

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Neptunyl NpO_2^{n+} complexes on the surface of goethite α-(FeOOH) resulted from the interaction of neptunyl nitrate (NpO_2NO_3, 10^{-6} M) in the aqueous media with the background electrolyte ($NaClO_4$) of ionic force 0.1 M (pH = 7.0   0.2) were formed and studied with the X-ray photoelectron spectroscopy. The X-ray photoelectron spectroscopy ionic and elemental quantitative analysis of the goethite and products of its interaction with neptunyl and plutonyl nitrates was carried out. It was established that during the studied neptunyl nitrate – goethite interaction Np^{4+} and Np^{6+} compounds did not to form, while the complexes of neptunyl group NpO_2^{1+} containing Np^{5+} ions with oxygen, water and/or carbonate ions in the equatorial planes did.

Key words: goethite, X-ray photoelectron spectroscopy, actinide, neptunyl

INTRODUCTION

Determination of physical and chemical states of radionuclides in the environment is one of the critical problems in the radioecology [1, 2]. It will help understand radionuclide absorption and migration mechanisms for development of technology of radioactive waste fixation, compacting, and disposal. X-ray photoelectron spectroscopy has proved to be the most adequate method for determination of radionuclide physical and chemical states [2]. This work conducted the X-ray photoelectron spectroscopy (XPS) study of goethite (α-FeOOH) and products of its interaction with neptunyl and plutonyl nitrates in aqueous media in order to understand the sorption and interface (natural water – mineral) interaction.

Migration behaviour of radionuclides depends on their physical and chemical states in the environment [1]. The processes on the border mineral-environment like oxidation-reduction, sorption and complex formation in many respects determine the radionuclides mobility. Neptunium in the environment presents basically as neptunyl NpO_2^+. Since it has a low charge, it is relatively chemically inactive. Under the environment influence this ion can transit into one of Np^{4+} or $Np(VI)O_2^{2+}$ forms [3].

Goethite (-FeOOH) is a prevalent natural mineral of high sorption ability to heavy metal ions and radionuclides. The present work studied the sorption mechanisms and $Np(V)O_2^+$ complexes on the surfaces of this mineral with the liquid-liquid extraction and X-ray photoelectron spectroscopy methods. The liquid-liquid extraction can separate neptunium ions of different oxidation states. XPS is the most adequate method for determination of radionuclide physical and chemical states. Earlier this method was used for the study of Cr^{6+} Cr^{3+} reduction on goethite surface [4], which was explained by the presence of Fe^{2+} traces, as well as

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Authors' addresses:
[1] Russian Research Center "Kurchatov Institute"
1, Kurchatov square, Moscow 123182, Russian Federation
[2] M. V. Lomonosov Moscow State University,
Chemical Dept., GSP-2, Leninskie Gory
Moscow 119992, Russian Federation
[3] Vernadsky Institute of Geochemistry and Analytical Chemistry
GSP-1, 19, Kosigina, Moscow 117975, Russian Federation
[4] Faculty of Natural Sciences and Mathematics,
University of Montenegro
P. O. Box 211, 81000 Podgorica, Serbia and Montenegro

E-mail address of corresponding author:
teterin@ignph.kiae.ru (Y. A. Teterin)

for the study of uranyl interaction with hydroxyl- and fluorine-apatite in aqueous media [5].

EXPERIMENTAL

The goethite sample α-FeOOH (Sample I) was synthesized from $Fe(NO_3)_3$ by the technique described in [6]: 50 g of $Fe(NO_3)_3$ $9H_20$ were solved in 825 ml of twice-distilled water and added to 200 ml of 2.5 M solution of KOH. The solution was mixed during 24 hours at 60 °C. The residuum was several times washed in twice-distilled water and acetone and dried at 40 °C during 2 days. For sorption experiments, suspension of -FeOOH was prepared.

Sample II was prepared from goethite -FeOOH suspension (Sample I) of the known concentration (0.0374 g, which corresponded to $1.6 \cdot 10^{18}$ nm^2 of the free surface and $5.2 \cdot 10^{-6}$ M of sorption centers) in the centrifuge test-tube. After this the background electrolyte ($NaClO_4$) of the ionic force 0.1 M was added. Then the standard $^{237}Np^{5+}$ solution ($NpO_2NO_3 \cdot nH_2O$) was added so that the total concentration was about 10^{-6} M. The solution was kept at pH = 7.0 0.2 and constantly mixed during several days in nitrogen atmosphere. The parent solution was separated by a centrifuge at about 100 rotations per second. After the sorption, the aliquot of the parent solution was collected. The sorption degree and neptunium distribution in the parent solution was determined by chemical methods described in [3] (method of liquid extraction). The saturation was done several times. The extraction of neptunium showed the presence of only $^{237}Np^{5+}$. A 30% saturation of goethite surface was reached. It corresponded to about $1.53 \cdot 10^{-6}$ M of $^{237}Np^{5+}$. The same sorption experiment was done 3 times. After the sorption and separation from the parent solution, the samples were dried in the vacuum for 30-35 hours. A similar technique was employed for preparation of Sample III, where plutonium ($^{242}Pu^{5+}$) in form of $PuO_2NO_3 \cdot nH_2O$ was used. Despite the fact that the spectrometer sensitivity did not allow to detect the Pu4f XPS peak, the present work gives the characteristic of the sample surface and evaluates the possible plutonium contents. These data also enables to evaluate the errors of the XPS measurements.

XPS spectra of the studied solid-state samples were taken with an MK II VG Scientific spectrometer at $1.3 \cdot 10^{-7}$ Pa at a room temperature. Overall resolution measured as the $Au4f_{7/2}$ electron line full width at half maximum was better than 1.2 eV. Electron binding energies (E_b) are given relative to that of the C1s electrons from adventitious hydrocarbons at the sample surface defined as 285.0 eV. The error in determination of E_b was 0.1 eV, and that of line intensities – 10% [7]. Samples for the XPS studies were prepared as thick layers of ultradispersed but not ground powders on the adhesive tape attached to the titanium substrates.

For all samples the quantitative elemental analysis was carried out using the following ratio: $n_i/n_j = (S_i/S_j)(k_j/k_i)$, where n_i/n_j is the relative concentration of considered atoms, S_i/S_j is the relative intensity of the core electron lines of these atoms, and k_j/k_i is an experimental sensitivity coefficient. The present work used the following coefficients: 1.00 (C1s), 2.8 (O1s), 8.0 ($Fe2p_{3/2}$), 0.55 (Fe3s), 9.20 (Na1s), 2.92 (Cl2p), 40.0 ($Np4f_{7/2}$), 44.0 ($Pu4f_{7/2}$) [8]. The sensitivity coefficients for neptunium and plutonium were obtained by extrapolation of the corresponding coefficients for thorium and uranium [8]. For neptunium this value within the 20% error agrees with $k_i(Np4f_{7/2}) = 49.2$ for $Cs_2NpO_2Cl_4$ single crystal [7]. XPS spectra from some neptunium compounds were used for interpretation of those from the studied Samples II and III (tab. 1).

RESULTS AND DISCUSSION

The technique of determination of physical and chemical states of radionuclides in the environment used in this work is based on the traditional XPS parameters (core electron binding energies and line intensities) and fine spectral structure parameters such as: relative intensities of the Fe3d and Np5f electrons weakly participating in the chemical bond, relative binding energies of the outer (OVMO) and inner (IVMO) valence molecular orbitals, multiplet splitting ΔE_{ms} [eV] of the core levels, dynamic effect related fine spectral structure parameters, relative binding energies of shake-up satellites ΔE_{sat} [eV] [7, 10]. These spectral data provide the important information about physical and chemical states of iron and actinides on the surface of the studied samples.

Low binding energy spectral range. Valence band of goethite α-FeOOH (Sample I) lies in the binding energy range 0-40 eV and consists of the OVMO (0-15 eV) and IVMO (15-40 eV) lines (fig. 1a). The peak in the O2s binding energy range is relatively wide (O2s) = 4.4 eV, while the structured O1s peak is only 2.6 eV wide. This evidences that the O2s atomic orbital (AO) participate in the formation of molecular orbitals (MO). Indeed, the uncertainty ratio $\Delta E \Delta \tau$ h/2π, where ΔE – full width at half maximum of the level from which an electron was removed, $\Delta \tau$ – lifetime of the hole and h – Plank's constant, gives that if the O2s level had been atomic, it would have been narrower than the O1s one. However, the experimental data contradict it. Therefore, the O2s level is not atomic, it is MO related.

Valence band of goethite α-FeOOH is mainly due to the MOs from the Fe3d,4s and O2s,2p elec-

Table 1. Neptunium oxidation states (Np^{n+}) and electron binding energies (E_b, eV) for Samples I, II, III, and neptunium compounds [7]

Sample(a)	Np^{n+}	MO	$Fe2p_{3/2,1/2}$(b)	Fe3s	$Np4f_{7/2,5/2}$	O1s	C1s
Sample I (α-FeOOH)		6.9 22.9	711.6 (719.8) 725.1 (733.4) (743.3)	93.6 101.0		530.3 531.5	285.0 288.6
Sample II (α-FeOOH + Np^{n+})	Np^{5+}	7.1 23.7	711.9 (720.2) 725.5 (733.4) (743.1)	94.2 101.2	403.6 415.2	530.5 531.5 533.1	285.0 288.3
Sample III (α-FeOOH + Pu^{n+})		6.4 23.4	712.0 (720.2) 725.5 (733.4) (743.0)	94.5 101.5		530.4 531.7 533.7	285.0 289.0
NpO_2	Np^{4+}				402.5 414.3	529.7	284.5
$RbNpO_2(NO_3)_2\ 2H_2O$	Np^{5+}	2.9 (Np5f) 5.4 27.0			403.6 415.3	531.5 533.5	285.0
$Cs_2NpO_2(CH_3COO)_3$	Np^{5+}	2.3 (Np5f) 4.3 27.2			403.0 414.6	531.5	285.0 288.3
$Cs_3NpO_2Cl_4$	Np^{5+}	2.5 (Np5f) 4.9 26.2			403.4 415.2	531.6	285.0
$Cs_2NpO_2Cl_4$	Np^{6+}	3.3 (Np5f) 5.3 25.8			404.6 416.4	531.9	285.0
$NaNpO_2(CH_3COO)_3$	Np^{6+}	3.4 (Np5f) 5.9 24.2 26.0			405.2 417.0	532.0	285.0 288.8

(a) Samples I, II, and III were prepared on the adhesive tape, the other samples – in indium
(b) Satellite binding energies are given in parenthesis

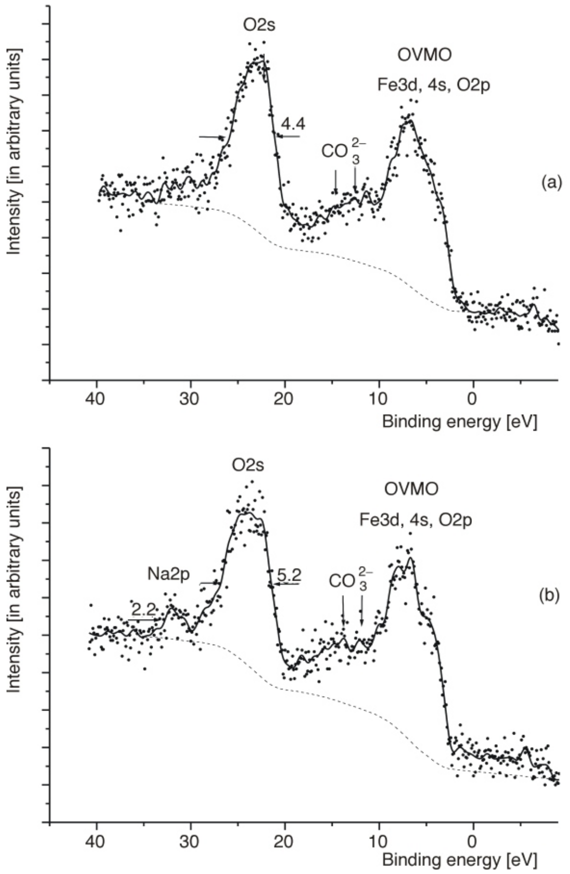

Figure 1. XPS spectra of the low binding energy electrons from: (a) – goethite α-FeOOH (Sample I), (b) – product of interaction of goethite with NpO_2NO_3 in aqueous media (Sample II)

tronic levels of the neighboring iron and oxygen. The OVMO structure is mainly due to the Fe3d,4s – O2p interaction, while the IVMO structure – Fe3p,3d,4s – O2s interaction [9]. Since iron electronic configuration is {Ar}$3d^6 4s^2$, where {Ar} – argon electronic configuration, and the Fe3d photoemission cross-section is much higher than the O2p one [11], the OVMO intensity is expected to come from the $Fe3d^5$ electrons of the basic Fe^{3+} state (fig. 1a). Unfortunately, this spectrum does not allow a correct quantitative evaluation of the Fe3d intensity and the number of the Fe3d electrons. The low intense structure at 12-14 eV can be attributed to the MO electrons of the carbonate CO_3^{2-}-group [9].

The low binding energy spectra from product of goethite-neptunium interaction (Sample II) exhibit some changes due to the surface changes under the influence of the solution (fig. 1b). In this case the Np5f peak is expected at E_b 2.5 eV. The intensity (area) of this peak is proportional to the number of the Np5f electrons weakly participating in the chemical bond, and quantitatively characterizes neptunium oxidation state in compounds. Unfortunately, this peak is feebly visible due to the low neptunium concentration. The low intense Na2p peak is observed at E_b = 32.2 eV. Going from Sample I to Samples II and III, a shoulder at the lower binding energy side at 5 eV becomes more distinctive. For Sample II unlike for Sample III, a certain widening of the line in the O2s range was observed.

Core electron spectral range. The sample surface can contain absorbed hydrocarbon, oxygen and water molecules. The available surface cleaning was not used in this work to avoid sample destruction. The C1s spectrum of Sample I (α-FeOOH) consists of the basic peak at E_b = 285.0 eV (saturated hydrocarbons), which is the reference peak used for calibration, a peak at E_b = 288.6 eV (CO_3^{2-} group) and a peak at E_b = = 275.4 eV due to $AlK_{\alpha 3,4}$ satellites (fig. 2a). These satellites are located on the lower binding energy side from the basic lines at 9.8 eV (7.33%) and 11.9 eV (3.66%) for $AlK_{\alpha 3}$ and $AlK_{\alpha 4}$ respectively, the relative satellite intensities are given in parenthesis [12]. For Sample II (-FeOOH + NpO_2NO_3) low intense extra lines at E_b = 279.1 eV and E_b = 282.8 eV are observed. They can be partially attributed to the $Np5p_{1/2}$ related structure due to the dynamic effect [7]. In this case, the dynamic effect can be considered as a phenomenon resulting in the extra two-hole state ($Np5p^6 5d^8 5f^{n+1}$) in addition to the basic one-hole state ($Np5p^5 5d^{10} 5f^n$) due to the gigantic Koster-Cronig electronic transitions between the core and outer levels [7]. It leads to the complex fine structure in the Np5p spectrum in the binding energy range 275–285 eV (fig. 2b).

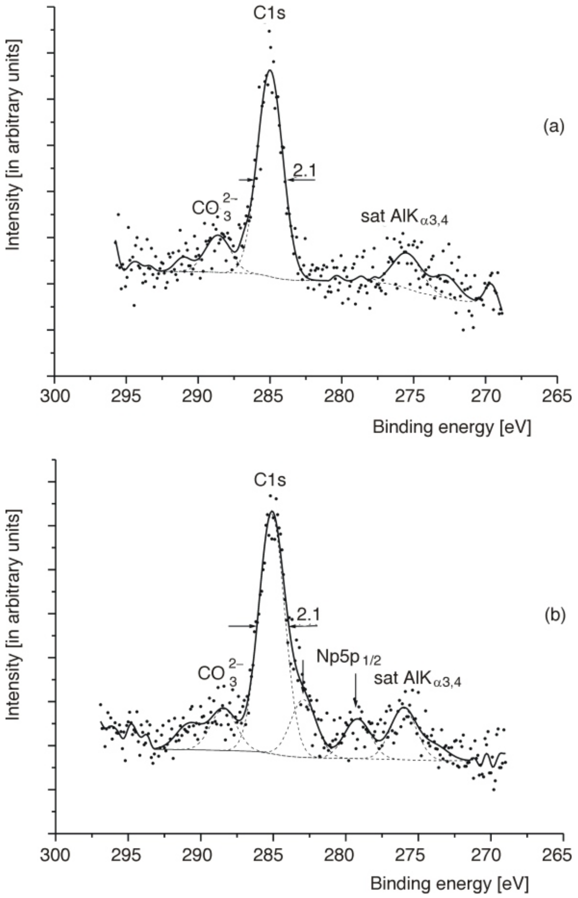

Figure 2. C1s XPS spectra from: (a) – goethite -FeOOH (Sample I), (b) – product of interaction of goethite with NpO_2NO_3 in aqueous media (Sample II)

The O1s spectrum from Sample I consists of a widened [(O1s)=2.6 eV] peak at E_b = 530.9 eV. This peak can be decomposed into the two components of about the same intensities (fig. 3a). The peak at E_b = 530.3 eV can be attributed to oxide, and the one at E_b = 531.5 eV – to hydroxide. It agrees with the corresponding binding energies 530.1 eV and 531.8 eV for -FeOOH [12]. During the interaction of goethite with NpO_2NO_3 in the water media, a redistribution of oxygen states on the surface was observed (fig. 3b). An extra water related peak E_b = = 533.1 eV appears. A similar, although significantly less intense, extra peak was observed also for Sample III with very low plutonium contents (formula III). While contents of the two main oxygen ion types in Sample I and III are about the same, the oxide-related oxygen in Sample II shows a tendency to decrease (formulas I-III). One of the reasons for the decrease of intensity at E_b = 530.5 eV can be, for example, the changes in the sample surface under the influence of the solution.

Despite the surface contamination with hydrocarbons, the core electron peaks are observed intense. The mathematical processing of the Fe2p spectra shows that these spectra are structured and can not be

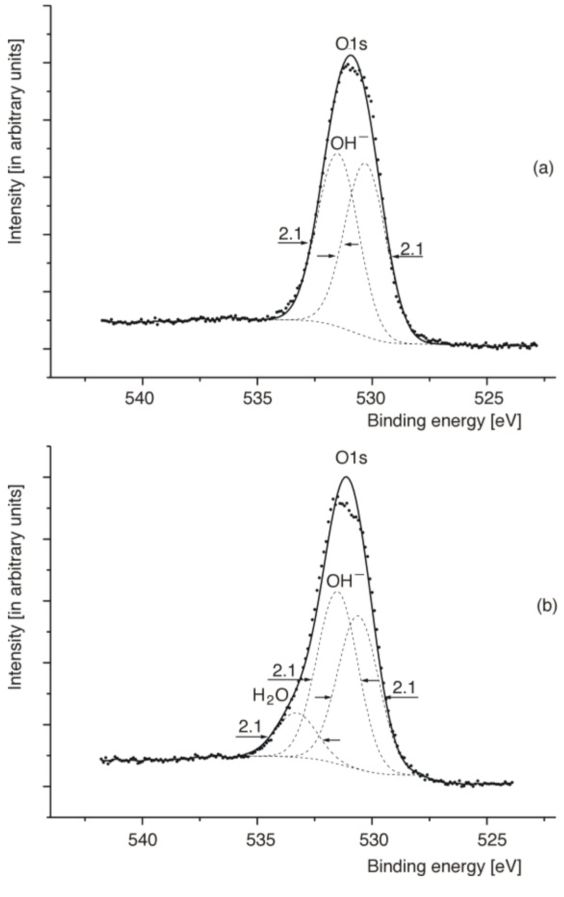

Figure 3. O1s XPS spectra from: (a) – goethite -FeOOH (Sample I), (b) – product of interaction of goethite with NpO_2NO_3 in aqueous media (Sample II).

decomposed in the separate components correctly because the Fe2p spectra exhibit with the high probability both multiplet splitting due to the presence of the uncoupled Fe3d^5 electrons in the ground state and the shake up satellites due to the extra excitations of electrons within the valence MOs during the Fe2p photoemission [10, 12].

The Fe2p$_{3/2}$ binding energy (Sample I) of 711.6 eV is slightly higher than the corresponding value 711.0 eV for -FeOOH given in [12]. The spin-orbit splitting from this spectrum is E_{sl} = = 13.5 eV and comparable with ΔE_{sl} = 13.2 eV for metallic iron [13]. On the higher binding energy side from the basic peaks the typical satellites at E_{sat1} = 8.2 eV and E_{sat2} = 18.2 eV (fig. 4a, tab.) are observed. Going to the spectra from Samples II and III, a shift (E_b = 0.3 eV and ΔE_b = 0.4 eV respectively) of the Fe2p$_{3/2}$ peak toward the higher binding energy and some changes in the spectral structure are observed (fig. 4b, tab.1). This shift can be due to the changes in iron oxidation state under the influence of the solution.

The Fe3s spectrum from goethite -FeOOH (Sample I) instead of a single sharp peak shows a complex fine structure (fig. 5a). With the high probability this spectrum shows the multiplet splitting of E_{ms} = 7.4 eV. This splitting is proportional to 2S + 1, where S – total spin of the ion, or to the number of the uncoupled Fe3d^5 electrons [10, 12]. The intensity ratio of the doublet has to be I_1/I_2 = = (S + 1)/S, *i. e.* 7/5, which agrees with the experimental value. In reality, the structure of this spectrum is more complex. Since the condition E_b(Fe3s) $2E_b$(Fe3p) is satisfied, there is a certain probability of an extra state after the photoemission of the Fe3s electron (dynamic effect [10, 12, 14]). It results in formation of the Fe^{3+} final states like: Fe3s^{1}3p^{6}3d^5 (one-hole state) and Fe3s^{2}3p^{4}3d^6 (extra two-hole state). It can complicate significantly the spectra, which increases the error of the multiplet splitting measurement. As an example of the possible structure, the present work gives the decomposition of this spectrum (fig. 5a). Since the dynamic effect has a resonance nature, as it was shown for barium compounds [14], the dynamic effect related structure can depend on the nature and location of ligand ions around iron. Despite this, the Fe3s spectrum enables to measure the multiplet splitting and determine the number of the uncoupled electrons with a reasonable error. This splitting

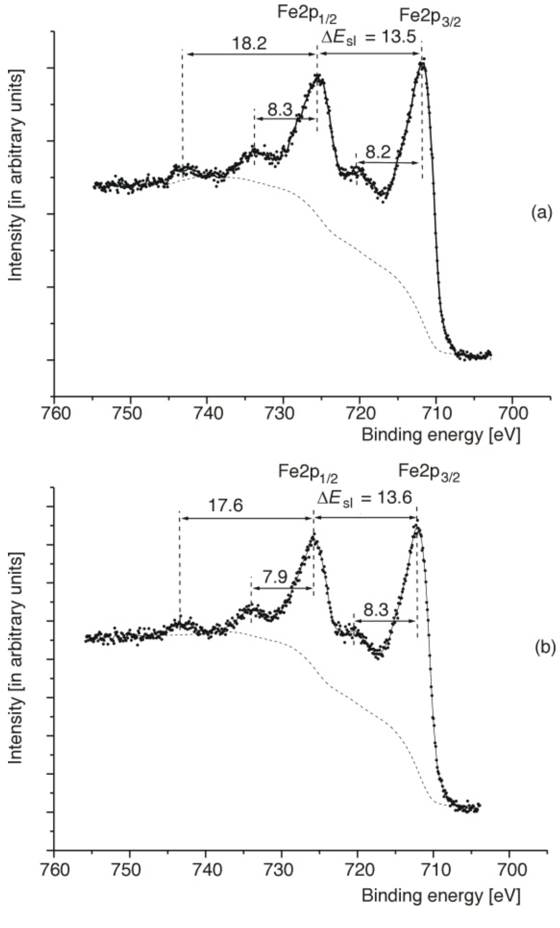

Figure 4. Fe2p XPS spectra from: (a) – goethite -FeOOH (Sample I), (b) – product of interaction of goethite with NpO$_2$NO$_3$ in aqueous media (Sample II)

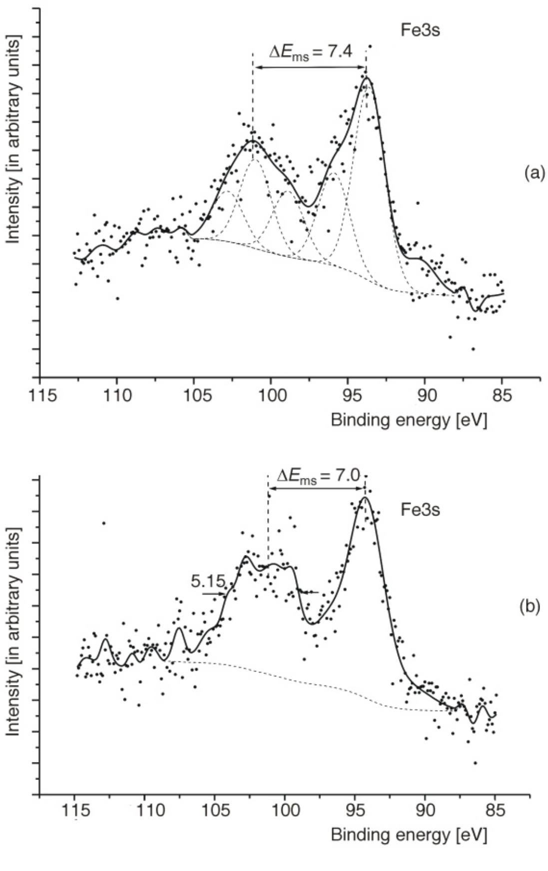

Figure 5. Fe3s XPS spectra from: (a) – goethite -FeOOH (Sample I), (b) – product of interaction of goethite with NpO$_2$NO$_3$ in aqueous media (Sample II).

for Samples II and III was measured to be $E_{ms} = 7.0$ eV (fig. 5b, tab.1). The difference in the spectral structures of Samples I and II can be attributed to a certain change in iron surrounding on the surface under the influence of the solution (fig. 5). In ionic approximation this spectral structure shows that Fe^{3+} ions present on the sample surfaces.

The Np4f spectrum consists of the spin-orbit doublet ($\Delta E_{sl} = 11.6$ eV) of relatively sharp peaks (fig. 6a). The binding energy $E_b(Np4f_{7/2}) = 403.6$ eV is closer to those 403.4 eV and 403.6 eV in $Cs_3NpO_2Cl_4$ and $RbNpO_2(NO_3)_2\,2H_2O$ containing Np^{5+} ions (tab. 1). The Na1s peak is observed at $E_b(Na1s) = 1073.1$ eV (Sample II), while the Cl2p one of perchlorate group ClO_4^{1-} and the N1s one of NO_3^{1-} group are nor detected (*i. e.* Cl and N concentrations are less than 1 at.%). At $E_b(Cl2p_{3/2}) = 199.6$ eV (Sample II) a low intense Cl2p peak was observed. It can be attributed to NaCl (formula II). The $Pu4f_{7/2}$ binding energy and spin-orbit splitting are $E_b(Pu4f_{7/2}) = 428.7$ eV and $E_{sl}(Pu4f_{5/2}) = 12.5$ eV for $Cs_2PuO_2Cl_4$ single crystal. However, the spectrum from Sample III in this binding energy range does not show this doublet (fig. 6b), which indicates insufficient (undetectable by XPS) plutonium contents. On the basis of this data the upper border of plutonium concentration on the surface of Sample III was evaluated (formula III).

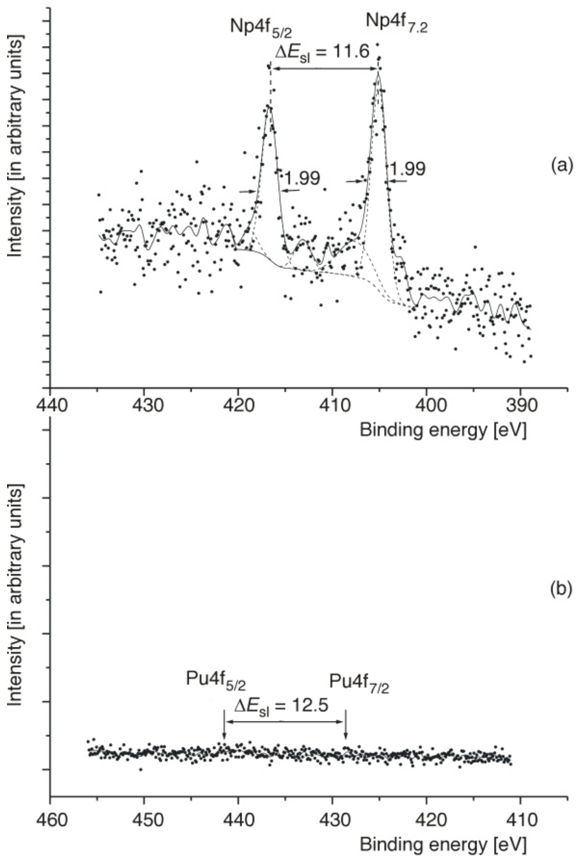

Figure 6. An4f XPS spectra from the product of interaction of goethite with AnO_2NO_3 in aqueous media: (a) – Np4f (Sample II), (b) – Pu4f (Sample III)

Results of the quantitative analysis. The error in determination of quantitative elemental and ionic compositions of the studied samples (Samples I, II, III) grows because of the complex spectral structure due to the multiplet splitting and secondary electronic processes (many-body perturbation and dynamic effect) and can exceed 10%. Since many-body perturbation results in the shake up satellites on the higher binding energy side from the basic peaks, the satellite intensities can be partially taken into account (fig. 4). However, it is difficult to take into account the dynamic effect related decrease of intensity. But the dynamic effect does not influence significantly on the considered spectra. Since the Fe2p spectrum is complicated, the present work used the Fe3s peak for the quantitative analysis. The sample surfaces were found to have the following compositions relative to one iron ion:

(Sample I)
$Fe_{1.00}O^{I}_{1.12}(O)O^{II}_{1.12}(OH^{1-})C^{I}_{0.23}(CH_{3-})C^{II}_{0.04}(CO_3^{2-})$

(Sample II)
$Fe_{1.00}O^{I}_{0.91}(O)O^{II}_{1.03}(OH^{1-})O^{III}_{0.26}(H_2O)Np_{0.003}$
$(Np^{6+})Na_{0.08}Cl_{0.03}C^{I}_{0.28}(CH_{3-})C^{II}_{0.03}(CO_3^{2-})$

(Sample III)
$Fe_{1.00}O^{I}_{0.92}(O)O^{II}_{0.92}(OH^{1-})O^{III}_{0.04}(H_2O)Pu_{(<0.0001)}$
$C^{I}_{0.55}(CH_{3-})C^{II}_{0.05}(CO_3^{2-})$

where $O^{I}(O)$, $O^{II}(OH^{1-})$, and $O^{III}(H_2O)$ – oxygen ions of oxide, hydroxyl group, and water. The observed oxygen excess in Sample I and II can be partially attributed to oxygen-containing molecules absorbed on the surface and high measurement error. Despite the fact that neptunium concentration in Sample II is about 1/1000 (0.1 at.%), the XPS method allows a reliable determination of neptunium oxidation state (fig. 6a). The interaction of goethite with neptunyl ions can be suggested to take place via hydroxide oxygens of goethite located in the equatorial plane of NpO_2^{5+} ion.

CONCLUSIONS

(1) Neptunyl NpO_2^{n+} complexes on the surface of goethite α-FeOOH resulted from the interaction of neptunyl nitrate NpO_2NO_3 (10^{-6} M) in the aqueous media with the background electrolyte ($NaClO_4$) of ionic force 0.1 M (pH = 7.2 ± 0.2) were formed and studied with the X-ray photoelectron spectroscopy.

(2) The XPS ionic and elemental quantitative analysis of the goethite and products of its interaction with neptunyl and plutonyl nitrates was carried

out. It was established that during the studied neptunyl nitrate – goethite interaction Np^{4+} and Np^{6+} compounds did not to form, while the complexes of neptunyl group NpO_2^+ containing Np^{5+} ions with oxygen, water and/or carbonate ions in the equatorial planes formed.

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Јуриј А. ТЕТЕРИН, Степан Н. КАЛМИКОВ, Александар П. НОВИКОВ,
Јуриј А. САПОЖЊИКОВ, Лабуд ВУКЧЕВИЋ, Антон Ј. ТЕТЕРИН, Константин И.
МАСЛАКОВ, Игор О. УТКИН, Икуле Б. ХАСАНОВА, Наталија С. ШЧЕРБИНА

ИСПИТИВАЊЕ ИНТЕРАКЦИЈЕ Np^{5+} СА ГЕТИТОМ α-FeOOH МЕТОДОМ РЕНДГЕНОМ ИНДУКОВАНЕ ФОТОЕЛЕКТРОНСКЕ СПЕКТРОСКОПИЈЕ

Нептунил NpO_2^{n+} комплекси на површини гетита α-(FeOOH), настали из интеракције нептунил нитрата (NpO_2NO_3, 10^{-6} M) у воденој средини, са основним електролитом ($NaClO_4$) јонске јачине 0.1 M (pH = 7.0 ± 0.2), били су награђени и испитивани методом рендгеном индуковане фотоелектронске спектроскопије. Извршена је елементарна квантитативна анализа гетита и продуката његове интеракције са нептунил и плутонил нитратима. Утврђено је да се током испитивања интеракције нептунил нитрат – гетит, не граде Np^{4+} и Np^{6+} једињења. Комплекси нептунил групе NpO_2^{1+} који садрже Np^{5+} јоне са кисеоником, водом и/или карбонатним јонима, граде та једињења у екваторијалним равнима.

Кључне реч: гетит, рендгеном индукована фотоелектронска спектроскопија, актиниди, нептунил